Note

Dimension-dependent two-electron Hamiltonian matrix elements

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Since the birth of quantum mechanics the ground state electronic energy of the two-electron atom has received special attention. This is because the two-electron system is the simplest atom to include electron–electron interactions. These interactions are key to understanding many-electron systems. This paper adds to the knowledge of two-electron atoms by presenting closed form solutions for Hamiltonian matrix elements at arbitrary spatial dimension, D. The basis functions are the D-dependent hydrogenic wavefunctions: $\{1s^2, 2p^2, 3d^2, 4f^2\}$. The electron–electron repulsion integrals are solved by the Fourier integral transform.

1. Introduction

The calculation of the ground state properties of two-electron atoms has received attention since the 1920's [7,12]. Once the two-electron problem is fully in hand, the knowledge gained can be applied to many-electron systems. The purpose of this paper is to extend the knowledge of two-electron atoms by presenting dimension-dependent electron–electron repulsion integrals in closed form. Not surprisingly, this advance has been made possible by computers. In particular, symbolic algebra programs such as MATHEMATICA [11] enable involved Fourier integral transforms to be done.

2. The basis set

The Schrödinger equation generalized to arbitrary spatial dimension, D, written in atomic units and neglecting nuclear motion, is

$$\left(-\frac{1}{2}\sum_{\nu=1}^{D}\frac{\partial^2}{\partial r_{1\nu}^2} - \frac{1}{2}\sum_{\nu=1}^{D}\frac{\partial^2}{\partial r_{2\nu}^2} - Z\left[\sum_{\nu=1}^{D}r_{1\nu}^2\right]^{-1/2} - Z\left[\sum_{\nu=1}^{D}r_{2\nu}^2\right]^{-1/2}\right.$$
$$\left. + \left[\sum_{\nu=1}^{D}(r_{1\nu}-r_{2\nu})^2\right]^{-1/2}\right)\Psi = E\Psi. \tag{1}$$

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In the limit of infinite dimension, with appropriate dimensional scalings [9], the two-electron atom takes the form of a rigid symmetric structure. The two electrons are equidistant from the nucleus and have an interelectron angle a little larger than $90°$ (e.g., $95.3°$ in helium). In this limit, all excited states are degenerate, and instead of orbitals we have a fixed geometry. As we back away from this limit, and D takes on a large but finite value, the electrons begin to oscillate as in a symmetric triatomic molecule. The simplest approximation takes the vibrations as harmonic and thus separable in normal coordinates. The normal coordinates are a symmetric stretch, an antisymmetric stretch, and a bend [5].

Within the orbital approximation, the two stretching coordinates, r_S and r_A, are related to fluctuations in the hydrogenic radii, r_1^0 and r_2^0, by a $45°$ rotation. Thus, the vibrational eigenstates, involving only the stretching coordinates, can be related to conventional representations in terms of hydrogenic orbitals, involving only s orbitals [8].

Excited vibrational eigenstates involving the bending coordinate θ, on the other hand, are related to conventional configurations with $l_1, l_2 \neq 0$. We impose the restriction of spherical symmetry so that we treat only D-dependent S-states. That is, the orbital angular momentum quantum numbers for the electrons must be equal. Since the orbital angular momentum is the same for each electron, the addition of one quantum of angular vibration corresponds to $n \to n + 1$ and $l \to l + 1$ for each electron, where n is the principal quantum number and l is the orbital angular momentum quantum number. Thus, the purely angular vibrational spectrum at high-D corresponds to the orbital configurations of $1s^2$, $2p^2$, $3d^2$, $4f^2$, $5g^2$, etc.

We now consider the basis functions $1s^2$, $2p^2$, $3d^2$ and $4f^2$ for arbitrary D. The angular dependence is given by Gegenbauer polynomials in $\cos\theta$. These polynomials are an orthogonal set with respect to the volume element, $\sin^{D-2}\theta$. Combining these polynomials with D-dependent radial wavefunctions gives the first four (unnormalized) basis functions:

$$\phi_{1s^2}(\mathbf{r}_1, \mathbf{r}_2, z, D) = \exp\left[-\kappa z(r_1 + r_2)\right],$$

$$\phi_{2p^2}(\mathbf{r}_1, \mathbf{r}_2, z, D) = \exp\left[-\kappa^2 z(r_1 + r_2)/(\kappa + 1)\right](\mathbf{r}_1 \cdot \mathbf{r}_2),$$

$$\phi_{3d^2}(\mathbf{r}_1, \mathbf{r}_2, z, D) = \exp\left[-\kappa^2 z(r_1 + r_2)/(\kappa + 2)\right]$$
$$\times \left[D(\mathbf{r}_1 \cdot \mathbf{r}_2)^2 - r_1^2 r_2^2\right],$$

$$\phi_{4f^2}(\mathbf{r}_1, \mathbf{r}_2, z, D) = \exp\left[-\kappa^2 z(r_1 + r_2)/(\kappa + 3)\right]$$
$$\times \left[(D + 2)(\mathbf{r}_1 \cdot \mathbf{r}_2)^3 - 3(\mathbf{r}_1 \cdot \mathbf{r}_2)r_1^2 r_2^2\right], \qquad (2)$$

where $\mathbf{r}_1 \cdot \mathbf{r}_2 = (r_1^2 + r_2^2 - r_{12}^2)/2$, $\kappa = (D-1)/2$ and z is an effective nuclear charge. The κ terms in the exponentials render the most probable radius dimension-independent.

We have only singlet states, so the spin portion of the wavefunction is $[\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2}$. We multiply this spinfunction by all our spatial wavefunctions.

With the basis set chosen, we move on to calculating integrals, the Hamiltonian matrix elements.

3. The matrix elements

Applying the Hamiltonian of equation (1) to our basis functions yields three types of integrals:

- Integrals that involve the Laplacians and have the form

$$G_{mn} = G\big(mk^2, nl^2\big) = \int d^D r_1 \, d^D r_2 \, mk^2(\mathbf{r}_1, \mathbf{r}_2)$$
$$\times \left(-\frac{1}{2} \sum_{\nu=1}^{D} \frac{\partial^2}{\partial r_{1\nu}^2} - \frac{1}{2} \sum_{\nu=1}^{D} \frac{\partial^2}{\partial r_{2\nu}^2} \right) nl^2(\mathbf{r}_1, \mathbf{r}_2). \quad (3)$$

- Integrals that involve the electron–nucleus interaction and have the form

$$I_{mn} = L\big(mk^2, nl^2\big) = \int d^D r_1 \, d^D r_2 \, mk^2(\mathbf{r}_1, \mathbf{r}_2)$$
$$\times \left(-Z \left[\sum_{\nu=1}^{0} r_{1\nu}^2 \right]^{-1/2} - Z \left[\sum_{\nu=1}^{0} r_{2\nu}^2 \right]^{-1/2} \right) nl^2(\mathbf{r}_1, \mathbf{r}_2). \quad (4)$$

- Integrals that involve the electron–electron interaction and have the form

$$J_{mn} = J\big(mk^2, nl^2\big) = \int d^D r_1 \, d^D r_2 \, mk^2(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{r_{12}} nl^2(\mathbf{r}_1, \mathbf{r}_2), \quad (5)$$

where

$$\frac{1}{r_{12}} = \left[\sum_{\nu=1}^{D} (r_{1\nu} - r_{2\nu})^2 \right]^{-1/2}.$$

In these integrals, $mk^2(\mathbf{r}_1, \mathbf{r}_2)$ and $nl^2(\mathbf{r}_1, \mathbf{r}_2)$ are the D-dependent two-electron ^1S basis functions in equation (2).

The first two types of integrals, G_{mn} and I_{mn}, are straightfoward. This is because the operators and the wavefunctions are all for hydrogen-like atoms. For hydrogen [8], we have

$$E_n^{(D)} = -\frac{(D-1)^2}{2(D+2n-3)^2}, \quad (6)$$

in which n is the principal quantum number. By simple scaling arguments,

$$\big\langle T_n^{(D)} \big\rangle = -2z^2 E_n^{(D)} \quad \text{and} \quad \big\langle V_n^{(D)} \big\rangle = 4zZ E_n^{(D)}. \quad (7)$$

Combining equations (3), (4), (6) and (7) yields

$$G_{nn} = \frac{z^2(D-1)^2}{(D+2n-3)^2} \quad \text{and} \quad I_{nn} = -\frac{2zZ(D-1)^2}{(D+2n-3)^2}. \quad (8)$$

We are only concerned with the $m = n$ case. When $m \neq n$, these integrals are zero since hydrogen-like wavefunctions are orthogonal.

The J_{mn} integrals are not as straightforward. At $D = 3$, one popular procedure is to separate the radial variables from the angular variables. Then, the angular integral can be solved using the spherical harmonic expansion

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m_l=-l}^{+l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_l^{m_l}(\theta_1, \varphi_1) Y_l^{m_l*}(\theta_2, \varphi_2), \tag{9}$$

where $r_<$ and $r_>$ are the smaller and larger of r_1 and r_2, respectively. The number of terms in equation (9) that actually need to be considered is limited to a finite number by restrictions on the angular momentum couplings. When equation (9) is used to solve the angular integral, the angular momentum coupling coefficients that result are found by group theory [1,2].

The angular portion of the J_{mn} integrals can also be solved by group theory at $D = 4$. Unfortunately, there is no similar group theoretic extension to higher dimensions at the present time [13]. As a result, instead of the spherical harmonic expansion, we use the Fourier integral transform method to evaluate the electron repulsion integrals [3].

The D-dimensional Fourier transform of $1/r_{12}$ is [10]

$$\frac{1}{r_{12}} = \frac{\Gamma[(D-1)/2]}{2\Gamma(1/2)\pi^{D/2}} \int d\mathbf{t} \, \frac{e^{i\mathbf{t}\cdot(\mathbf{r}_1-\mathbf{r}_2)}}{t^{D-1}}. \tag{10}$$

Utilizing this transform, choosing $\mathbf{t}$ parallel to the $\mathbf{z}$ axis, and using only spherically symmetric states, the specific integrals that must be solved are

$$\begin{aligned}
J_{mn} = {}& \frac{\Gamma[(D-1)/2]}{2\Gamma(1/2)\pi^{D/2}} C_D C_{D-1} \int_0^{\infty} \frac{d^D t}{t^{D-1}} \\
& \times \int_0^{\infty} d^D r_1 \, d^D r_2 \, r_1^{D-1} r_2^{D-1} \, mk^2(\mathbf{r}_1, \mathbf{r}_2) nl^2(\mathbf{r}_1, \mathbf{r}_2) \\
& \times \int_0^{\pi} d\theta_1 \sin^{D-2}\theta_1 \, e^{itr_1\cos\theta_1} \int_0^{\pi} d\theta_2 \sin^{D-2}\theta_2 \, e^{itr_2\cos\theta_2}.
\end{aligned} \tag{11}$$

The quantity C_D is defined as [6]

$$C_D = \frac{2\pi^{D/2}}{\Gamma(D/2)}. \tag{12}$$

The angular and radial integrals can be found in integral tables for $m = n = 1$. However, when excited states are treated, the angular integrals soon become too difficult in this coordinate system. In order to continue to find the matrix elements analytically, we follow Herrick and Stillinger [4] and define our new coordinate system as

$$u = r_{12}, \qquad s = r_2 + r_1, \qquad t = r_2 - r_1. \tag{13}$$

The integrands can now be expanded in terms of the functions $e^{-ks/2}s^p u^q t^r$, where k is a scale factor. In this new coordinate system, the volume element is

$$d\tau = u(s^2 - t^2)\left[(s^2 - u^2)(u^2 - t^2)\right]^{(D-3)/2} ds\, du\, dt, \tag{14}$$

and all the matrix elements for the ground state energy are sums of

$$
\begin{aligned}
B_D(k, p, q, r) &= \int_0^\infty ds \int_0^s du \int_0^u dt \\
&\quad \times e^{-ks} s^p u^q t^r u(s^2 - t^2)\left[(s^2 - u^2)(u^2 - t^2)\right]^{(D-3)/2} \\
&= \frac{\Gamma(a)}{4k^a} B\left(\frac{q + r + D - 1}{2}, \frac{D-1}{2}\right) B\left(\frac{r+1}{2}, \frac{D-1}{2}\right). \tag{15}
\end{aligned}
$$

In this equation, $a = p + q + r + 2D - 3$ and $B(b, c) = \Gamma(b)\Gamma(c)/\Gamma(b + c)$ is the beta function.

To illustrate this method, consider the matrix element $\langle 2p^2|1/r_{12}|2p^2\rangle$. Switching to the new coordinate system gives us

$$
\begin{aligned}
\phi_{2p^2}(r_1, r_2, z, D) &= \exp\left[-\kappa^2 z(r_1 + r_2)/(\kappa + 1)\right](\mathbf{r}_1 \cdot \mathbf{r}_2) \\
&= e^{-ks/2}(s^2 + t^2 - 2u^2)/4, \tag{16}
\end{aligned}
$$

where $k = (D-1)^2 z/(D+1)$. With this wavefunction, the unnormalized matrix element is

$$
\frac{1}{16}\int_0^\infty ds \int_0^s du \int_0^u dt\, e^{-ks}(s^2 + t^2 - 2u^2)^2(1/u)u(s^2 - t^2) \\
\times \left[(s^2 - u^2)(u^2 - t^2)\right]^{(D-3)/2}. \tag{17}
$$

Expanding the integrand yields a sum composed of eight $B_D(k, p, q, r)$ integrals. Each one is solved using the beta function expression of equation (15).

To get the normalization factor, the $1/u$ term is dropped from equation (17). This increases the value of q by one in equation (15). Thus, the normalization is simply the eight $B_D(k, p, q, r)$ integrals we already have except q is increased to $q + 1$. This normalization factor is divided into the first result and we have solved the matrix element.

What is required is a simple expression for the numerator, which involves the $1/u = 1/r_{12}$ operator, and for the denominator, the normalization. For the numerator, equation (15) simplifies to

$$
\begin{aligned}
&B_D^{\text{num}}(k, p, q, r) \\
&= \frac{(D-1)D\Gamma[(D-1)/2]\Gamma(2D + p + q + r - 3)(1/2)_{r/2}[(D-1)/2]_{(q+r)/2}}{4k^a\Gamma(D+1)(D-1)_{(q+r)/2}(D/2)_{r/2}}, \tag{18}
\end{aligned}
$$

where the subscripts of quantities in parentheses or brackets indicate Pochhammer symbols. And for the denominator,

$$B_D^{\text{den}}(k, p, q, r)$$
$$= \frac{(D - 1/2)\Gamma(D/2)\Gamma(2D + p + q + r - 2)(1/2)_{r/2}(D/2)_{(q+r)/2}}{4k^{a-1}\Gamma(D + 1/2)(D - 1/2)_{(q+r)/2}(D/2)_{r/2}}. \quad (19)$$

Only four matrix elements based on these formulas are available in the literature. They are $\langle 1s^2|1/r_{12}|1s^2\rangle$ [4], $\langle 2s^2|1/r_{12}|2s^2\rangle$, $\langle 2s^2|1/r_{12}|2p^2\rangle$ and $\langle 2p^2|1/r_{12}|2p^2\rangle$ [3]. One reason for so few results may be that when the integrand is expanded, the number of terms grows rapidly. For example, $\langle 4f^2|1/r_{12}|4f^2\rangle$ generates a polynomial of 94 $B_D(k, p, q, r)$ integrals. Computer programs that are able to manipulate algebraic expressions of this length are relatively new.

For calculations using the $\{1s^2, 2p^2, 3d^2, 4f^2\}$ basis set, eight more matrix elements are needed. These additional matrix elements were found to be

$$\langle mk^2|1/r_{12}|nl^2\rangle = C_{mn}Q_{mn}R_{mn}S_{mn}T_{mn},$$

with

$$Q_{mn} = \frac{D - 1}{[(D + 2m - 3)(D + 2n - 3)]^{1/2}},$$

$$R_{mn} = \frac{\zeta_m^{D+2m-2}\zeta_n^{D+2n-2}}{[(1/2)(\zeta_m + \zeta_n)]^{2D+2m+2n-5}},$$

$$S_{mn} = 2^{m+n-3/2}\frac{\Gamma(D/2 + m + n - 3/2)\Gamma(D + m + n - 3/2)}{\Gamma(D/2)\Gamma(D + 2m + 2n - 3)},$$

$$T_{mn} = \left[\frac{(n-1)!}{2(m-1)!}\right]^{1/2}\frac{\Gamma(n - m + 1/2)}{\Gamma(1/2)(n-m)!}, \quad (20)$$

Table 1
C_{mn} values.

m	n	C_{mn}
1	1	1
1	2	$D^{-1/2}$
1	3	$(D - 1)^{1/2}D^{-1}(D + 2)^{-1/2}$
1	4	$(D - 1)^{1/2}D^{-1/2}(D + 2)^{-1}(D + 4)^{-1/2}$
2	2	$4^{-1}(4D^2 + 15D - 7)D^{-1}(D + 1)^{-1}$
2	3	$8^{-1}(D - 1)^{1/2}(8D^2 + 55D + 27)D^{-3/2}(D + 1)^{-1}(D + 2)^{-1/2}$
2	4	$12^{-1}(D - 1)^{1/2}(12D^2 + 119D + 149)D^{-1}(D + 1)^{-1}(D + 2)^{-1}(D + 4)^{-1/2}$
3	3	$32^{-1}(D - 1)(32D^4 + 528D^3 + 2665D^2 + 4092D + 1755)D^{-2}(D + 1)^{-1}(D + 2)^{-1}$ $\times (D + 3)^{-1}$
3	4	$32^{-1}(D - 1)(32D^4 + 728D^3 + 5371D^2 + 13960D + 11445)D^{-3/2}(D + 1)^{-1}(D + 2)^{-3/2}$ $\times (D + 3)^{-1}(D + 4)^{-1/2}$
4	4	$128^{-1}(D - 1)(128D^6 + 4896D^5 + 72236D^4 + 517965D^3 + 1877495D^2 + 3280323D$ $+ 2185965)D^{-1}(D + 1)^{-1}(D + 2)^{-2}(D + 3)^{-1}(D + 4)^{-1}(D + 5)^{-1}$

where $\zeta_m = [(D+2n-3)/(D+2m-3)]^{1/2} z_m$ and $\zeta_n = [(D+2m-3)/(D+2n-3)]^{1/2} z_n$. Recalling equations (2), z_m and z_n are the effective nuclear charges. The C_{mn} values are given in table 1.

References

[1] L.C. Biedenharn, J. Math. Phys. 2 (1961) 433.
[2] R.D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, CA, 1981) p. 366.
[3] D.R. Herrick, J. Math. Phys. 16 (1975) 1047.
[4] D.R. Herrick and F.H. Stillinger, Phys. Rev. A 11 (1975) 42.
[5] D.R. Herschbach, J. Chem. Phys. 84 (1986) 838.
[6] H. Hochstadt, *The Functions of Mathematical Physics* (Wiley, New York, 1971) p. 171.
[7] E.A. Hylleraas, Z. Phys. 48 (1928) 469; 54 (1929) 347.
[8] J.G. Loeser, Ph.D. dissertation, Harvard University (1984).
[9] M. López-Cabrera, A.L. Tan and J.G. Loeser, J. Phys. Chem. 97 (1993) 2467.
[10] M. Luban and A. Baram, J. Chem. Phys. 76 (1982) 3233.
[11] *MATHEMATICA* (Wolfram Research, 1996).
[12] J.C. Slater, Phys. Rev. 31 (1928) 333.
[13] C.E. Wulfman, in: *Group Theory and Its Applications*, Vol. 2, ed. E.M. Loebl (Academic Press, New York, 1971) p. 164.